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Assessing the (In)Stability of Urban Art Paints: From Real Case Studies to Laboratory Investigations of Degradation Processes and Preservation Possibilities

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Abstract: Urban art as a shared expression of street art between artists, citizenship and municipalities has always had an important role in the social life and appearance of modern cities. However, the durability of urban and street artworks is susceptible to the degradation processes that the employed commercial paint formulations undergo once outdoors. These are complex mixtures of compounds, differently sensitive to environmental agents according to their chemical nature. Starting from the colorimetric analysis of murals created in 2010, 2011 and 2018 in Reggio Emilia, Italy, documenting their degradation already after a few months, this study aimed at understanding the stability of the most unstable paints used by the artists in these artworks. A multi-analytical approach evaluated the commercial products under the chemical point of view, after natural and accelerated ageing. Additionally, two manufactured anti-UV varnishes were evaluated for their possible use as coatings. The results pinpointed the weaknesses of the selected paints and highlighted how the application of an anti-UV coating might slightly affect the visual aspect of the artwork, though ensuring a greater resistance to the outdoor conditions due to their minor chemical sensitivity to environmental agents.

Keywords: street and urban art; spray paints; acrylic paints; alkyd; degradation of modern art; anti-UV varnishes

Citation: Cimino, D.; Lamuraglia, R.; Saccani, I.; Berzioli, M.; Izzo, F.C. Assessing the (In)Stability of Urban Art Paints: From Real Case Studies to Laboratory Investigations of Degradation Processes and Preservation Possibilities. *Heritage* **2022**, *5*, 581–609. https://doi.org/10.3390/heritage5020033

Academic Editor: Francesco Soldovieri

Received: 19 February 2022
Accepted: 21 March 2022
Published: 24 March 2022

1. Introduction

Raised as a protest and social expression on city and railway walls, street art has now become a vivid tool for urban redevelopment [1], thus the most befitting name is urban art. Urban art festivals are more often organised, and city halls call upon famous or emerging artists to dress their streets to be "painted cities", such as Sant'Angelo di Roccalvecce, Cibiana di Cadore, Orgosolo Dozza or Maglione in the Italian case. Around Europe, degraded areas of Heerlen, Belgrade, Antwerp, Bristol, Malmo, Reykjavik, Budapest and other cities are becoming, thanks to urban art, more attractive neighbourhoods. At the same time, artworks of artists, such as Blu, Banksy, Millo, Amara, and C215, even when not authorised, are considered part of the contemporary art heritage, and, for this reason, issues about their preservation and conservation are being raised. The main questions are devoted to better understanding the complex interactions between art materials and the substrates they are applied on. Most contemporary materials (i.e., primers, paints, varnishes, and coatings) are based on polymeric matrices with the addition of several organic and inorganic components (pigments, fillers, and additives) whose chemical natures define the relative stability to the environment, particularly in outdoor conditions. Environmental agents (i.e., moisture, rain, temperature and its excursion, pollutants, and sunlight among all) are likewise enemies of urban artworks [2,3], especially those on building facades [4–6].

On the other side, the substrate plays an important role since, often, it is not adequate as a preparation layer for painting. Indeed, street art festivals consider the preparation of surfaces by the flattening of the surface and the application of primers, but in most cases, especially those not authorised, degradation phenomena are already ongoing (e.g., rising damp, salt efflorescence, detachment of plasters, and rust) [6–9].

Recently, research in heritage and conservation science has focused on the evaluation of the chemical and physical stability of the employed materials, and thus their durability against outdoor conditions, especially spray paints [10,11]. Mostly, accelerated artificial ageing tests have been carried out to study the degradation kinetics of the most employed commercial paints, such as Montana Colors (Barcelona, Spain), Lascaux (Brüttisellen, Switzerland), Molotow (Lahr/Schwarzwald, Germany) [6,12–14]. Attention has been drawn on natural ageing and real cases as well, but the majority of these projects are interested in the protection of this recent form of urban art against graffiti: indeed, urban art artworks are often subjected to undesired overpainting realised with similar materials and thus, are difficult to be removed without impairing the artwork as well [15]. For such a reason, studies have been addressed in two directions: the evaluation of chemical and mechanical removal of graffiti from street artworks surfaces and the evaluation of anti-graffiti coatings [15–22]. Nevertheless, the research assessed the instability toward UV-light and outdoor conditions of spray paints, and therefore, the proposal of anti-UV coatings to be applied on top of paint layers to ensure that they last longer, in an urban-adornment-maintaining perspective, should be deepened as well.

The present research raised real conservation issues encountered on murals created in Reggio Emilia (Italy) in different recent times by several artists: in 2010 by the Proyecto Ritual collective for Cooperative of Mancasale and Coviolo Popular Houses (artworks entitled “The Big Mother”, “Big Sacral Bird”, “Oriental Carpet”, “Economy subdues you”); in 2011 by Gola Hundun for the PIGAL community centre (artwork entitled “Two dragons carrying an egg—new creature”); in 2018 by Ivan Pontevia and Daniele Castagnetti for the Secondary School Dalla Chiesa (artwork entitled “UBUNTU”).

These artworks showed evident degradation phenomena ongoing in a relatively short time: for “UBUNTU”, in particular, the deterioration was visible after seven months (Figure 1).

Figure 1. “UBUNTU” by Ivan Pontevia and Daniele Castagnetti in July 2018 (**left**) and in February 2019 (**right**).

Considered emblematic real cases, they were selected for the European project CAPuS—Conservation of Art in Public Spaces (ERASMUS+—Knowledge Alliances). The comparison of the current state with pictures taken just after the realisation has established that the most outstanding degradation phenomenon is a widespread chromatic alteration of the paint layers configured both as a total or partial fading or as a consistent chromatic change (e.g., from orange to a greyish-purple shade) (Figure 2). This is most evident for some orange, red and pink areas, compromising details and peculiar features of the image and, therefore, the total appearance of the artwork. This deterioration was associated with the employed commercial formulations [23]. The artists Gola Hundun, H101, Zosen, Kenor, Ivan Pontevia and Daniele Castagnetti used both spray and water-based paints for outdoor application spread with a roller and, in some cases, by brush. Mainly paints from MNT94 (Montana Colors, Barcelona, Spain) and Montana Cans (Heidelberg, Germany) commercial spray series were chosen, as confirmed by archive documentation (e.g., invoices and pictures of the realisation phases; see Appendix A, Figures A1 and A2). This allows to settle the present research.

Figure 2. "Economy subdues you" by Zosen in 2010 (**left**) and 2019 (**right**): strong chromatic alteration and fading (total or partial).

Indeed, the observation of the rapidity with which the many materials used have degraded from the aesthetic and material point of view highlighted the need to study these dynamics in depth. Thus, multi-analytical investigations were performed on five of the paints employed by the artists' collective. This approach involved a deep chemical characterisation of the formulations through spectroscopic, thermal, and chromatographic analyses, together with the evaluation of paint–film surface properties, such as their colour, wettability and morphology. These considerations were made on the commercial formulations as sold and after natural and accelerated ageing tests to investigate how different environmental conditions (in particular temperature, relative humidity, UV-light versus time of exposure) might affect the paints.

Moreover, the characterisation of two anti-UV coatings was performed, and the evaluation of the aesthetical modifications due to their applications on painted layers was considered. Indeed, in the last years, research has been addressed on the development and evaluation of anti-graffiti systems, overlooking the scarce resistance to UV light of contemporary paints, and probably referring to possible UV stabilisers in paint formulations and their resistance to this degradation agent.

2. Materials and Methods

2.1. Selection of Paints and Anti-UV Varnishes

Whereas this study aims at gaining a better understanding of the materials currently used by the artists mentioned and their contemporaries, laboratory experimentation has considered five commercial paints as declared to be used in Reggio Emilia.

Manufacturers of spray paints offer artists anti-UV varnishes. Among these, two formulations were tested, investigating their stability under the same ageing conditions, and evaluating the effect of their application over the painting layers. The choice took into account the declared chemical composition of spray paints, and thus, similar binders were selected, i.e., acrylic-based and alkyd-based ones.

All the details are listed in Table 1.

Table 1. List of selected materials within the experimentation.

Product Acronym	Product	Manufacturer	Declared Composition
PO	G2080 Pure Orange (spray)	Montana Cans (Heidelberg, Germany)	Nitrocellulose–acrylic–alkyd lacquer base
NF	MTN 94 Fluorescent Orange/Naranja Fluorescent (spray)	Montana Colors (Barcellona, Spain)	Modified alkyd resins
FR	Framaquarz TR NCS 3060-R	Lechler (Como, Italy)	Acrylic resin and quartz
OM	MTN 94 Frame Gold/Oro Marco (spray)	Montana Colors (Barcellona, Spain)	Modified alkyd resins
MA	MTN 94 RV-4010 Magenta (spray)	Montana Colors (Barcellona, Spain)	Modified alkyd resins
Anti-UV1	T1000 VARNISH GLOSS	Montana Cans (Heidelberg, Germany)	Nitrocellulose-acrylic resin
Anti-UV2	MTN PRO Synthetic Varnish	Montana Colors (Barcellona, Spain)	Alkyd-based resin

Mock-Ups Preparation

To study and evaluate the stability of the selected commercials products, a thin layer of each paint was applied on a microscope glass slide; the application of the products was via spray, except for the quartz-based paint FR, which was applied by brush because it was not supplied in a canister and was used this way, as introduced, by artists in Reggio Emilia.

After casting, specimens were kept in a horizontal position and dried under room conditions (20 ± 2 °C, 55 ± 3 RH%). After that, they were stored under controlled humidity in a desiccator until a constant weight was reached. This was reached after 30 days (considered as the casting time) and was considered the starting point for further evaluation of the morphological, chemical–physical, and thermal changes.

To test their stability, thin layers of anti-UV protective varnishes were prepared and characterised as well, before and after ageing. Moreover, to evaluate how the application of the anti-UV coating could induce variation in terms of colorimetric and surface aspects of commercial paints, stratified samples were made by the application of two layers of the coating on top of a colour. For this part of the research, only spray paints were considered, as their use is most common by artists. The choice of the anti-UV coatings was based on the declared composition of the spray paints, and the application followed the manufacture instructions; therefore, an acrylic-based varnish was applied on acrylic paints, and likewise for alkyd colours (Table 1).

Two sets with all types of samples on slides (V) (i.e., only paint, only varnish, and stratigraphy) were organised and underwent natural (N) and accelerated ageing (A), respectively, to investigate product stability (Table 2). Two samples of each set were not aged, keeping those as references.

Table 2. List of samples considered in this study.

	Anti-UV Protective Varnish	
Paint	**Without Varnish**	**With Varnish**
PO	V-PO VN-PO VA-PO	VN-PO-AntiUV2 VA-PO-AntiUV2
NF	V-NF VN-NF VA-NF	VN-NF-AntiUV1 VA-NF-AntiUV1
FR	V-FR VN-FR VA-FR	-
OM	V-OM VN-OM VA-OM	VN-OM-AntiUV1 VA-OM-AntiUV1
MA	V-MA VN-MA VA-MA	VN-MA-AntiUV1 VA-MA-AntiUV1

2.2. Ageing Conditions

2.2.1. Natural Ageing

Natural ageing was performed from November 2019 to January 2020 (92 days in total) in Venice, Italy, placing samples outside the laboratory, exposed in the outdoor natural environment. The values of relative humidity (RH%), temperature (T), rainfall and irradiance were acquired from the ARPAV (Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto-Veneto Regional Agency for Environmental Prevention and Protection) [24] and are reported in Figure 3. Samples were placed in open boxes in a vertical position, simulating real case studies of street artworks painted along external walls. Thus, they were potentially exposed to rainfall, wind, and freeze—thaw cycles, but the orientation ensured no stagnation of water.

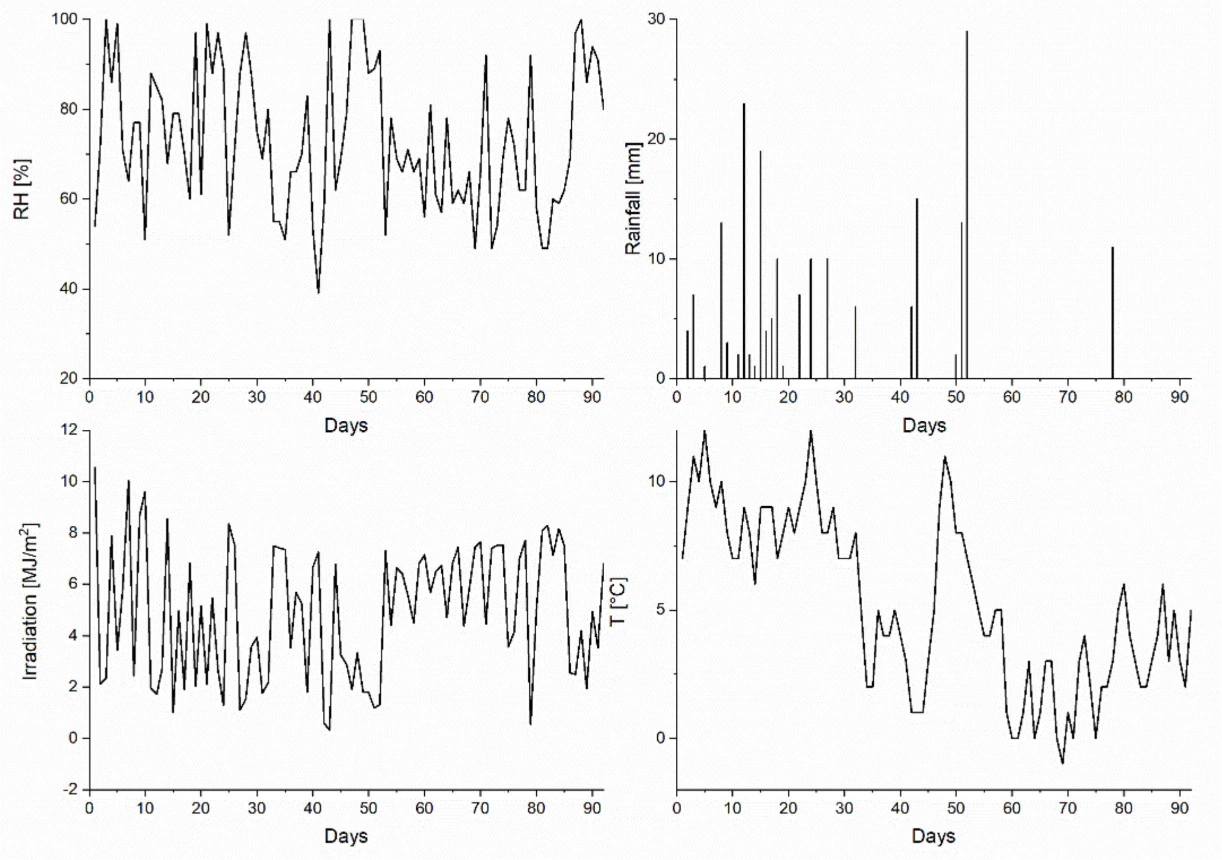


Figure 3. Weathering environmental condition of natural ageing test (ARPAV Venice–data collection at 18 a.s.l., Istituto Cavanis, November 2019–January 2020) [23]; clockwise: relative humidity, rainfall, temperature, and irradiation.

2.2.2. Accelerated Ageing

Accelerated ageing was carried out with a Q-Sun Xe-3 test chamber (Q-Lab) equipped with 3 Xenon lamps for a total of 1240 h, moving mock-ups every 256 h in the four quarters of the samples tray to avoid possible lightening differences among lamps that simulate sun irradiation. The ageing followed a two-step cycle, repeated 10 times: 100 h of light (radiant energy set at 68 W/m^2), 35 °C and environment relative humidity (RH, approximately 30%) followed by 24 h of dark, at 45 °C and 95% of RH.

Artificial ageing was performed using specific and deliberately extreme conditions to speed up degradation processes; phenomena were monitored after 5 cycles (620 h) and at the end of the 10 cycles (1240 h) through spectroscopic and chromatographic analyses and contact angle measurements.

2.3. Analytical Methods

The selected commercial products were characterised, and their stability monitored following a chemical–physical multi-analytical approach, as specified in the next sections.

2.3.1. Colorimetric Measurements

A Konica Minolta (Chiyoda, Tokyo, Japan) CM 2600 d spectrophotometer was employed to evaluate chromatic variations before and after ageing. The instrument has an 8-degree viewing angle geometry, with a diffusion light Xenon lamp and a high-resolution monolithic polychromator. The analysed area is circular, of 3 mm diameter and the considered results are the average of three measurements carried out on different points over the mock-up.

Measurements were performed in the CIELAB1976 space, and data were collected in SCI and SCE modalities (specular component included and excluded, respectively), since both can provide information about morphological changes (smoother/rougher surface) and molecular chemical changes that can promote colour variation [25]. Results are the average of three measurements and were elaborated by Spectra Magic NX 6. The total colour variation, expressed as ΔE, was calculated by Formula (1):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{1}$$

where ΔL^*, Δa^* and Δb^* are the differences between the average calculated for the same sample, after and before ageing, both natural and accelerated.

In the field of heritage science, it is assumed that when the ΔE values are higher than 3, the chromatic difference is visibly detectable by the naked eye [26–28].

Analyses were carried out on paint layers and anti-UV coatings before and after accelerated ageing. Data were also collected after the application of the anti-UV coating on paints to evaluate how they affect the aesthetic aspect.

2.3.2. Contact Angle Measurements

The evaluation of the wettability of paint layers and its variation due to ageing and to the application of the protective coating was achieved by contact angle measurements carried out following the sessile water drop method according to the standard EN 15802:2010 [29]. Three measurements were performed for each mock-up, and the average value was calculated. The shape of the drop was documented photographically with a digital microscope (Section 2.3.3), and evaluation of the θ angle was carried out on the images thanks to the software Dino Capture 2.0.

2.3.3. Digital Microscopy

The samples' surface and contact angle measurements were performed with a portable microscope manufactured by Dino-Lite Digital Microscope (Almere, The Netherlands), equipped with visible and UV-light sources and a camera, which allowed the acquisition of pictures of the most significant details. The observation was useful to evaluate film homogeneity and ageing-induced morphological changes. Pictures were elaborated with DinoCapture 2.0 software.

2.3.4. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out with a Netzsch (Verona, Italy) 409/C instrument. Fragments of films of about 10 mg were heated in an open platinum crucible from 25 °C to 700 °C at a heating rate of 10 °C min^{-1} in an inert nitrogen atmosphere fluxed at a flow rate of 80 mL/min. Data were collected and elaborated with TA Netzsch software. This characterisation phase was helpful to estimate approximately the relative amounts of the organic (i.e., binder, stabilisers, organic pigments) and inorganic (fillers, inorganic pigments, if present) fraction, considering the higher heat stability of the inorganic one. The solid residue that remained at the end of the measurements was further analysed by infrared spectroscopy (Section 2.3.5) for the identification of inorganic components.

2.3.5. X-ray Fluorescence (XRF)

As part of the characterisation of paint formulations, qualitative elemental analysis in paint formulations was carried out as X-ray fluorescence with a Bruker (Billerica, MA, USA) Crono XRF spectrometer, equipped with a 50 kV X-ray source with a rhodium anode, an SDD detector, a CCD camera and two laser pointers to focus the beam on the proper position. Each analysis lasted 30 s and collected a signal from an area of 0.5 mm as diameter. As a qualitative analysis, the configuration saw 40 kV tension and 30 µA amperage.

2.3.6. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy analyses were performed with a portable Bruker (Billerica, MA, USA) ALPHA spectrometer equipped with an attenuated total reflection (ATR) modulus based on a single-bounce diamond ATR crystal. The obtained spectra were the average of 32 scans acquired in the spectral range 4000 ÷ 400 cm^{-1}. Acquisition and elaboration (baseline correction, evaluation of peaks, comparison with databases) were carried out with Opus 8.2.28 and Omnic 9. The analysis of the materials as applied on substrates and of their TGA residue gave a first insight of the chemical composition, in particular concerning binders, pigments and inorganic fillers; the technique is valuable for the evaluation of the effects of the induced degradation too, analysing samples during and at the end of the ageing tests and comparing these data with spectra at the initial state.

2.3.7. Raman Spectroscopy

Since in contemporary paint formulations, the amount of inorganic filler might be higher than in the amount of pigment, Raman analyses were carried out. The characterisation of paint formulations took advantage of the greater accuracy of this analytical technique in the discrimination between these components [23]. To do so, a BRAVO Handheld Raman spectrometer (Bruker, Billerica, MA, USA) was used. The instrument has two excitation laser sources (Duo LASER™ excitation system) at 758 and 852 nm [30,31]. A preliminary excitation step considers the slight shift of the excitation wavelength of both lasers to remove from the final spectrum as much as possible the background and interferences as for induced fluorescence, increasing the signal-to-noise ratio (sequentially shifted excitation—SSE™ algorithm). For avoiding saturation of the CCD detector system, measurements acquisition parameters were set automatically by the instrument software. Raman spectra were recorded in the 3200 ÷ 300 cm^{-1} range and were successively elaborated with Opus 8.2.28.

2.3.8. Pyrolysis Gas Chromatography Coupled with Mass Spectroscopy (Py-GC/MS)

A Frontier Lab 3030D pyroliser was used in combination with a Thermo Scientific (Waltham, MA, USA) Trace 1310 gas chromatograph and a Thermo Scientific ISQ mass spectrometer. The pyrolysis unit was directly connected with an HP5 MS column (length 30 m, inner diameter 0.25 mm, and stationary film thickness 0.25 μm) by a split connector. Helium (1 mL/min) was used as the carrier gas in combination with a temperature program of 50 °C (held 3 min) to 315 °C (held 3 min), and 10 °C/min. The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 290 °C, and the temperature of the ion source was 240 °C. Mass spectra were recorded from 29 to 600 AMU at a speed of 7 scans/s. The analysis was carried out on raw materials for further components characterisation and later after ageing, to study degradation processes, eventually occurred. A total of 5 μL of a 5% methanolic solution of tetramethylammonium hydroxide (TMAH) was added to approximately 80 μg of solid sample to promote total thermal decomposition of the binder chain, especially alkyds. Nonadecanoic acid was added as an internal standard to follow degradation products formation in a semi-quantitative way. The chromatographic analysis followed the spectroscopic one and, on the base of the obtained results, the flash pyrolysis was set at 600 °C for acrylates and 650 °C for alkyd resins, kept for 0.20 min. Chromeleon 7 software was used to control the whole measurement and process data, whereas AMDIS and NIST software were employed for the identification.

3. Results and Discussion

3.1. Paint Formulations Characterisation

The selected paints were fully characterised through a multi-analytical investigation. Table 3 reports the obtained results in terms of binding media, pigments, dyestuff, and additives detected in the rather complex commercial formulations.

Two main chemical classes were identified in the organic fraction related to binding media: acrylics and alkyd-based resins. In particular, the results highlighted that only the magenta paint MA has an alkyd-based formulation, which is derived from the polymerisation of a polybasic acid with a polyhydric alcohol, modified with vegetable oil. Py-GC/MS revealed the presence of terephthalic acid, ortho-phthalic acid, benzoic acid and pentaerythritol as the main compounds in the polyester fraction [32–34].

The chromatographic results show also the typical fatty acids of a drying oil: saturated monocarboxylic (such as palmitic and stearic), dicarboxylic (such as azelaic, suberic and sebacic) and unsaturated (e.g., oleic) acids. According to the molar ratio between palmitic and stearic acids (P/S = 3.2), the lipidic fraction is likely composed of sunflower and/or safflower oil, drying/semi-drying vegetable oils commonly used by XX and XXI centuries paint manufacturers [35–39].

Acrylic copolymers were identified in the quartz-red paint and the golden one (respectively FR and OM), whereas in the orange and in the fluorescent ones, these polymeric binders were modified with other resins (Table 3). As copolymers, mostly methylmethacrylate (MMA), n-butyl acrylate (nBA) and n-butyl methacrylate (nBMA) were found, with styrene (PO paint), nitrocellulose (PO and NF paints) and/or alkyd resin (PO paint). PY-GC/MS results allowed, in some cases, the identification of the co-monomers, thanks to the presence of oligomers; in others, several monomers were identified, but not their possible combination.

As concerns the identification of colouring agents, the complementary analytical approach through spectroscopic and chromatographic techniques allowed to mainly recognise organic pigments and dyestuff, such as anthraquinones (PR168 in FR paint, PO43 in PO paint), azo-arylides (yellows PY3, PY74 and PY83 in the orange formulation PO) and azo (PR48 in the magenta paint MA). The supposed low concentration of the colourant agent in NF paint, together with the fluorescent behaviour, did not allow its easy identification either by FTIR and Raman spectroscopies (due to scattering problems). Nevertheless, the peak at 811 cm^{-1} in the FTIR spectrum of (due to triazine ring in melamine [40]), together with the triazine-based and toluene–sulfonamide-based structures detected in the pyrogram, suggested a synthetic organic dyestuff supported by a triazine–toluene sulfonamide–paraformaldehyde polycondensation resin [41,42].

Py-GC/MS helped as well in the identification of most of the organic additives, among those several stabilisers, UV-absorbers, plasticisers, fluidifiers, antioxidants, adhesive promoters, glazing agents, biocides as listed in Table 2. In the case of plasticisers, phthalates are those identified in all the studied formulations, and in particular, dimethyl (DMP), diethyl (DEP), dibutyl (DBP) and di-isobutyl (DIBP) phthalate: these compounds are widely found in modern paints as reported in many previous studies [12,34,40,43].

Among inorganic additives, silicates were always detected as thickeners and/or fillers, flanked by calcium carbonate ($CaCO_3$) or titanium dioxide (TiO_2) in some cases, as highlighted by IR and Raman spectroscopic analyses of the residue after TGA. The amount of the inorganic fraction of the formulations resulted in being variable, from ca 15% of the orange paint up to 97% in the fluorescent paint.

Table 3. Summary of paint formulations chemical characterisation; identified compounds are classified into categories.

Sample Name	Binder(s)	Pigments/Dyestuff	Additives	TGA Residue 700 °C [%]	Contact Angles (θ)	Comments
PO	Nitrocellulose Styrene-nBA copolymer Alkyd resin (polyols, benzoic acid, pentaerythritol tri/tetramethyl ester)	PO43 PY3 PY74 PY83	Hexanedioic acid, bis(2-ethylhexyl) ester (DEHA) DMP DEP Silicates TiO_2 $CaCO_3$	14.3	99	The abundance of benzoic acid in the pyrogram suggests the presence of an alkyd resin based on iso-phthalic acid [11]
NF	Acrylic copolymer (MA, MMA, nBA, nBMA monomers and oligomers) Nitrocellulose	Organic colourant supported by triazine-toluene sulfonamide-paraformaldehyde polycondensation resin	Uniplex 108 Ethyl-p-toluene sulfonate DMP Castor wax Silicates (identified: talc) TiO_2	97.4	81	In the limited organic fraction (less than 3%), high plasticisers concentration. Py-GC/MS: several aromatic compounds lead to the hypothesis of an acrylic resin modified with styrene (no oligomers observed though). Despite the use of TMAH added for promoting thermal decomposition, the retention times and the mass spectra of the triazine compounds suggested they are due to fragmentation of the dyestuff.
FR	nBA-nBMA-MMA copolymer	PR168	Silicates (identified: quartz, kaolin/nacrite) $CaCO_3$ DMP	69.4	87	
OM	Acrylic copolymer (MMA, nBMA, EHA, OMA monomers)	Metal powders (Al, Cu, Fe)	DEP DBP DIBP Biphenyl Castor wax Silicates TiO_2 $CaCO_3$	50.0	74	Supposed alkyd-based product, it is instead an acrylic formulation plasticised with phthalates. Metal feature given by metallic powders, maybe with the contribution of organic colourant/iron oxides
MA	Orthophthalic oil-modified alkyd resin (terephthalic acid, ortho-phthalic acid methyl ester)	PR 48:2 or 48:8	Biphenyl DMP TiO_2	34.3	89	A relative high amount of suberic acid together with the molar ratios between azelaic (A), palmitic (P), oleic (O) and stearic (S) acids suggested the addition of a sunflower or safflower oil [39]; molar ratios calculated from pyrograms: A/P = 0.35 O/S = 1.42 P/S = 3.2

Contact angle measurements performed on paint films provided information about their hydrophilicity: looking at θ values, it is possible to consider that the paint surfaces are partially wettable, ranging from 74° (OM paint) to 89° (MA paint), except for the magenta formulation PO (θ = 99°), which is considered non-wettable [44,45].

These data confirmed the declared composition for three of the studied formulations: indeed, two Montana® Colours products, namely the golden OM and the fluorescent NF paints, were revealed to have an acrylic-based binder instead of an alkyd one.

3.2. Evaluation of Ageing Tests on Paints Formulations

After the characterisation, paints underwent ageing. To better explain the data obtained with ageing conditions, the average of the values recorded for the main degradation agents (RH, T, rain and irradiance) were calculated. Since ARPA and the ageing chamber provide, respectively, the irradiation (MJ/m^2) and the irradiance (W/m^2) information, conversion from W/m^2 to MJ/m^2 was made (J = Ws). Despite the same time intervals for both tests, the environmental conditions were very different.

For outdoor winter conditions, the calculated average values were RH 73%, T 5 °C, rain 2 mm, irradiation 4.9 MJ/m^2 daily. For the artificial ageing, the parameters were controlled using the control unit of the ageing chamber, resulting in the end with these average values: RH 44%, T 37 °C, irradiation 6.0 MJ/m^2 daily.

In the following sections, the obtained results are introduced, taking into consideration the morphological, colorimetric, physical–chemical changes occurring with natural and accelerated ageing. It was experimentally observed, after ageing, that surface morphology, contact angle values and colorimetric parameters changed. Even though yellowing phenomena interest polymeric binders as largely reported in the literature [46–52], this evaluation is only partially carried out in this context since the influence of the colouring agent on the b* colouring agent is predominant and not easy to be subtracted.

3.2.1. Natural Ageing

Table A1 (Appendix B) illustrates the pictures acquired with a digital microscope under visible (Vis) and UV-light, before and after both natural and accelerated ageing. As can be observed, the winter ageing condition did not affect the surface morphology of the paint films, neither macroscopically nor microscopically; only a slight darkening of the surface was microscopically observed in PO and FR paint films.

In general, no significant colour changes were registered after three months of exposure to environmental outdoor agents: paint films maintained a nearly homogeneous aspect, and the total colour variations (ΔE) are within the limit value (threshold considered 3), as depicted in Figure 4. The only exception is the total colour variation of the PO spray paint, with a ΔE = 4 in SCE mode, and a decrease in a* and b* values, most likely due to an initial fading of the yellow and orange organic dyestuffs identified within the paint formulation (PO43, PY3/74/83) (Table 2). Observing the variation of L*, a certain decrease was detected for acrylic-based paints (PO, FR and OM) confirming microscopical observations on PO and FR films. For NF paint, the opposite variation of this parameter can be linked with a partial fading of the triazine-based colouring agent.

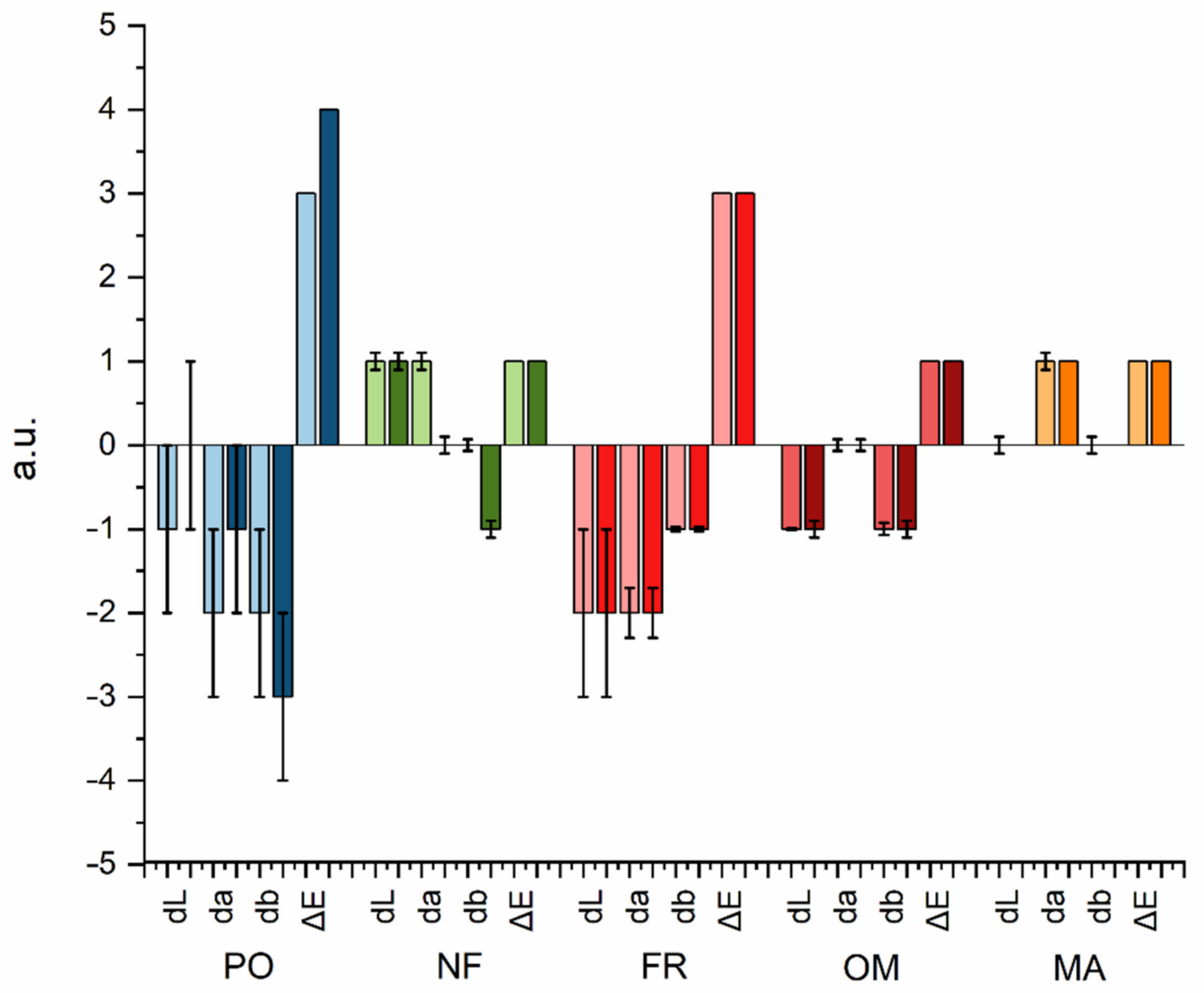


Figure 4. Comparison of colorimetric data in SCI (lighter) and SCE (darker) mode after natural ageing.

Chemical changes were evaluated through FTIR and Py-GC/MS analyses.

The most evident case of degradation interested the orange paint, PO, whose composition was found to be rather complex (a polystyrene n-butylacrylic paint combined with nitrocellulose and oil-modified alkyd resin). The FTIR results of Figure 5 with ageing, show the formation of hydroxylated species (an increase in OH band at 3350 cm^{-1}) together with the formation of unsaturation along the backbone chain and oxidised products (an increase in peak at 1646 cm^{-1} linked with inner double bonds and decrease in carbonyl peak at 1727 cm^{-1}), a clue of an ongoing chain-loss process and the presence in the aged film of ketones, anhydrides and carboxylic acids. The raise of a peak at 1770 cm^{-1} might suggest the presence of γ-lactones [53,54]. Py-GC/MS results corroborate FTIR findings, showing a progressive decrease in the amount of benzoic acid, a volatile compound which can be produced during styrene and alkyd polymeric chains degradation and/or can be present as a chain stopper. The pyrogram registered also the decrease in hexanedioic acid, bis(2-ethylhexyl) ester (DEHA); the hypothesis is that molecules of the plasticiser migrated to the surface, where they were washed away by rain action. Plasticisers migration is, indeed, a known phenomenon occurring in modern paint films [55,56].

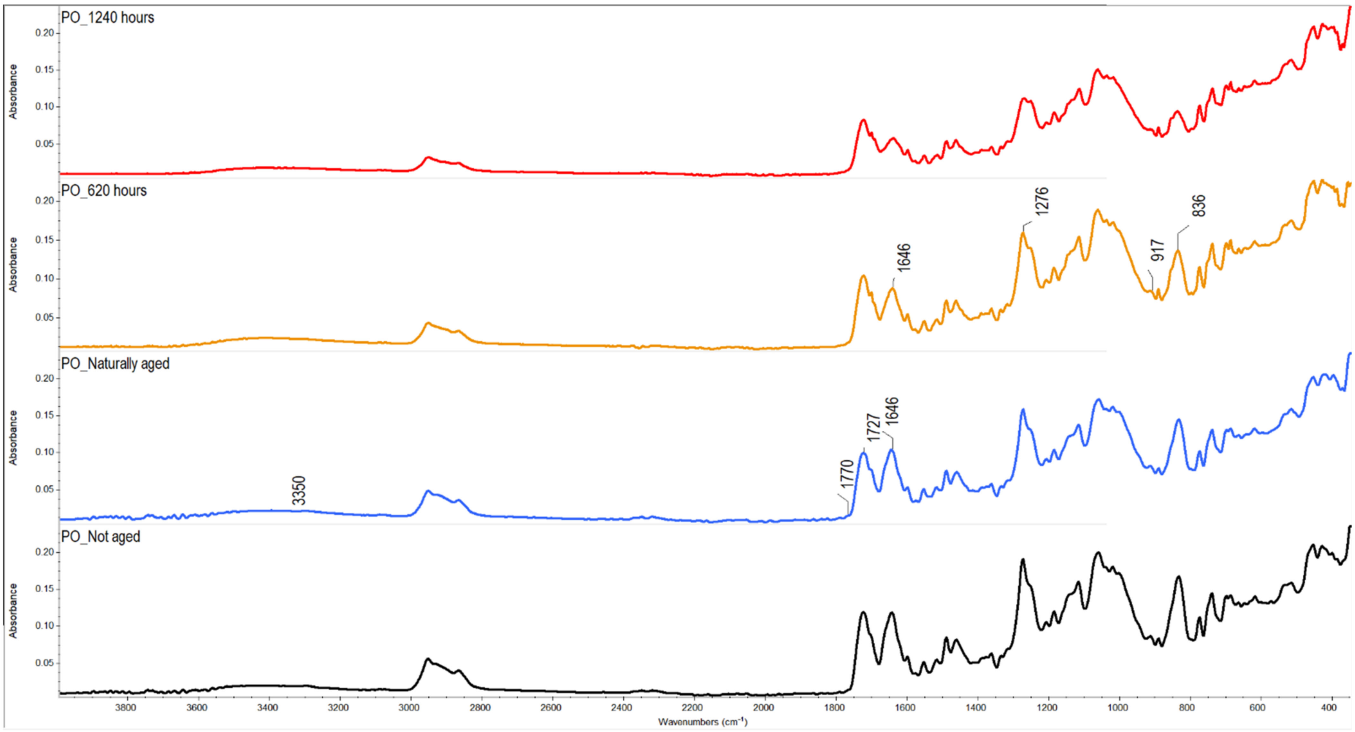


Figure 5. FTIR spectra of PO film before (lower) and after natural (blue line) and accelerated (orange line for the 620 h and red line for the 1240 h step, respectively) ageing.

These chemical modifications supported the colour variation, induced also by a probable yellowing of the binder.

The fluorescent paint NF did not show, in FTIR and Py-GC/MS data, particular chemical changes, despite a decrease in the intensity of the signals related to the dyestuff. NF contains a limited organic fraction in its formulation (ca 3% after TGA), and this makes it difficult to detect slight chemical modifications induced by short exposure to outdoor ageing conditions with the considered techniques.

Under these ageing conditions, also the quartz-based paint FR revealed to be stable from a chemical point of view. The FTIR spectra showed only a decrease in the intensity of the polymeric pattern, whereas from the chromatographic data, a decrease in the oligomers amount was detected. Similarly, lower concentrations of acrylic fractions were detected in the Py-GC/MS results of the metallic paint OM, while a general decrease in the FTIR spectrum pattern, where an increase in the OH band at high wavenumbers and a decrease in C=O (1723 cm^{-1}) and C-O (1143 cm^{-1}) bond peaks were observed. Furthermore, a decrease in the plasticisers signals was also registered by Py-GC/MS.

As occurred for the paint FR, the trend of the FTIR pattern of the magenta formulation MA showed a general decrease in the signals attributed to the binder. The relative pyrogram revealed a higher concentration of dicarboxylic acids (suberic and azelaic acids, in particular) together with a decrease in the unsaturated fatty acids (linolenic, linoleic and oleic acid). This is reflected in the molar ratios reported in Table 4: it can be observed that after natural and accelerated ageing tests, the azelaic to palmitic acids (A/P) ratios increased, while the oleic to stearic acids (O/S) decreased. As widely reported in the literature, these differences are linked to the oxidation and the curing processes occurring in the lipid fraction.

Table 4. Ratios between azelaic/palmitic (A/P) and oleic/stearic (O/S) acids as a method of evaluation of induced oxidation of lipid fraction of MA paint.

Ratio	Not Aged	Natural Ageing	Accelerated Ageing	
			620 h	1240 h
A/P	0.35	1.02	0.88	1.37
O/S	1.42	1.37	0.40	0.37

Aleuritic acid and oxidated species of octadecanoic fatty acids (epoxy-, oxo-, and methoxy-) were identified as well as oxidation by-products of unsaturated fatty acids present in the just applied film.

For the polyester fraction, a higher concentration of phthalic acid was observed, in parallel with a decrease in pentaerythritol, compared to the initial state. This is reported in the literature for the degradation of artistic alkyd paints [33,57,58].

Concerning wettability, it is not possible to identify a general trend of this property, and the variations in terms of θ values are not always consistent with the detected chemical variations (Figure 6 and Table 5). This is also because the Py-GC/MS technique analyses, the sample in bulk and with FTIR in ATR is not possible to isolate the contribution of the first film micrometres only. This implies that the effect of the migration of the additives or the degradation products toward the surface might affect only contact measurements. Fillers and inorganic additives may play an important role in it. The increase in contact angle values can be ascribable to the decrease in polar groups on the outer part of the film.

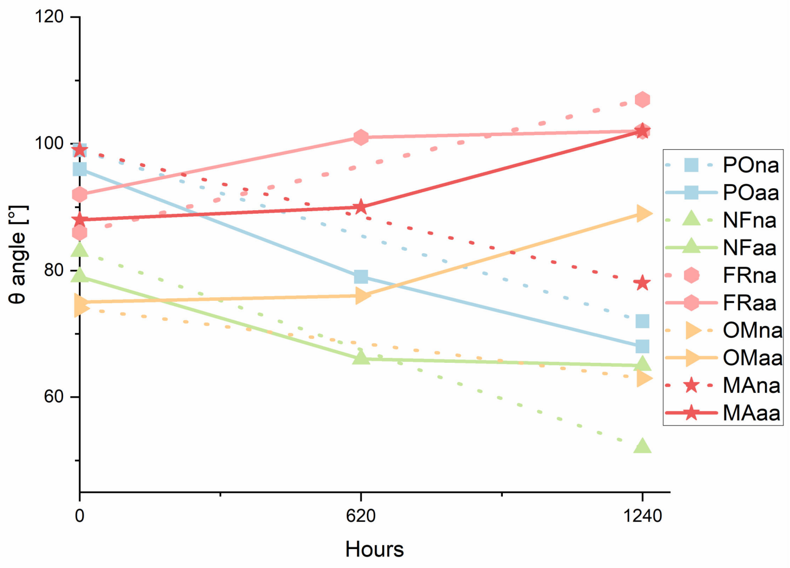


Figure 6. The trend of θ values during the ageing tests (natural—na; accelerated—aa).

Table 5. θ values (and relative standard deviation) before and after ageing tests followed by the total variations occurred.

Paint	Not Aged [θ]	Natural Ageing [θ]	Natural Ageing [Δθ]	Accelerated Ageing—1240 h [θ]	Accelerated Ageing—1240 h [Δθ]
PO	99 ± 5	72 ± 9	−27	68 ± 12	−31
NF	81 ± 7	52 ± 5	−29	65 ± 9	−16
FR	87 ± 9	107 ± 7	20	102 ± 3	15
OM	74 ± 4	63 ± 5	−11	89 ± 3	15
MA	89 ± 12	78 ± 12	−11	102 ± 5	13

In previous studies, an increase in contact angle was explained also by a micro-modification of the surface, in particular, in terms of the variation of roughness [47]. In this work, such modifications were not detectable with macro- and micro-observations; considering that the curing occurred in winter conditions and that during the ageing, some days rained, water mechanical effects might be at the base of the registered differences, together with the oxidation process.

3.2.2. Accelerated Ageing

Macroscopic and microscopic surface observations of PO, FR, OM and MA did not highlight evidence in morphological modifications of the films (Appendix B, Table A1). On the contrary, the film of the fluorescent NF paint was changed in appearance: indeed, the fading of the colour is remarkable, and, from a mechanical point of view, the film became brittle and fragile, being difficult to be manipulated. As highlighted by TGA, NF presented a ca 3% in weight referring to the organic fraction (mainly binder and plasticisers) and this can be associated with the ease of detachment of the film from the glass surface.

Moreover, it was also underlined by colorimetric measurements, as illustrated in Figure 7. Colour changes for NF were further proof of a severely induced degradation process that occurred already after 620 h of the solar box test and ended up with the highest calculated total colour variation, with a ΔE of about 80 at 1240 h. The variation of a* and b* parameters (Figure 8) is due to the fading of the fluorescent pigment, whose low lightfastness was declared by the Montana® Colours manufacturer, but also because of the contribution of the inorganic components identified (i.e., silicates and white pigment) which explains the shift in the colour parameters toward 0.

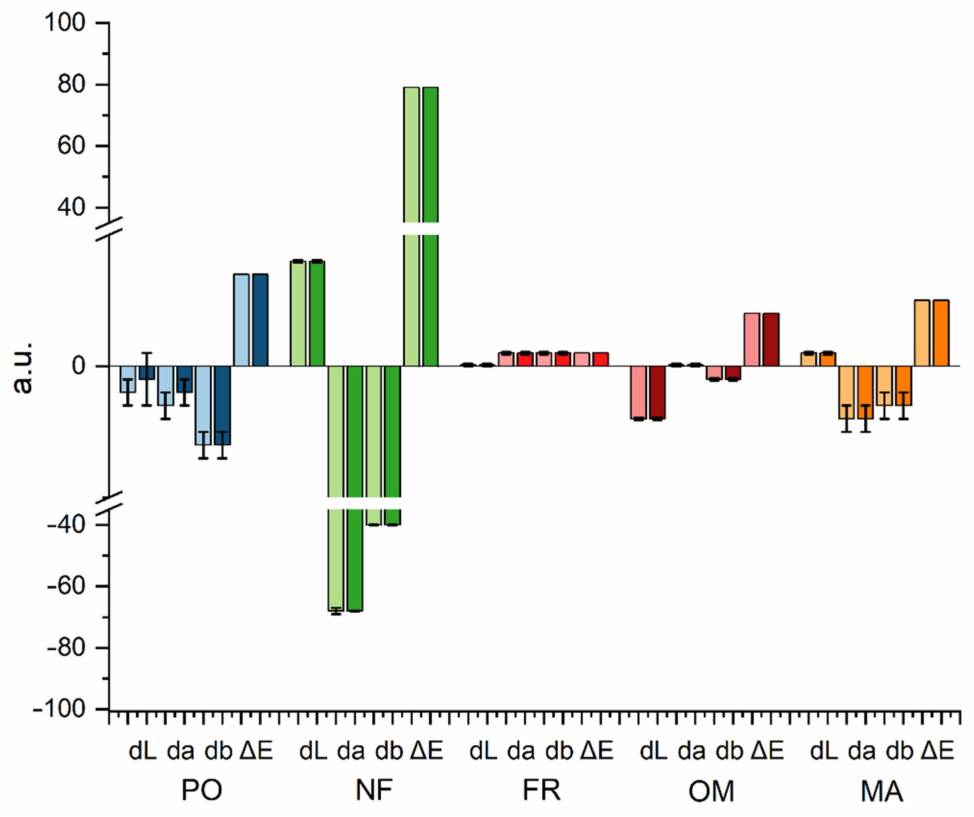


Figure 7. Comparison of colorimetric data in SCI (lighter) and SCE (darker) modes after accelerated ageing.

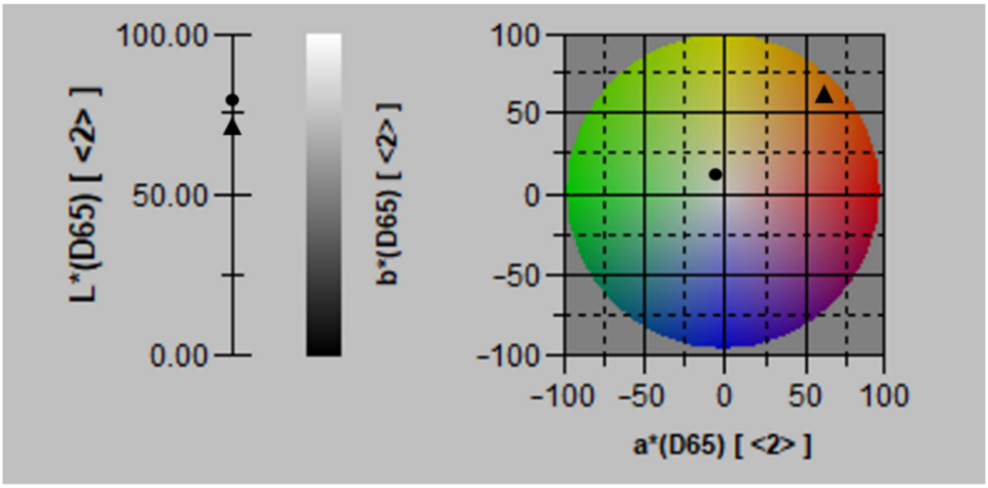


Figure 8. Colorimetric parameters for NF before (triangle) and after (circle) accelerated ageing test reported in the colorimetric space CIELab 1976.

The low lightfastness of this fluorescent spray paint was also observed in situ on the "UBUNTO" artwork: after only 7 months from the realisation, the flag was faded and, in some cases, almost disappeared (Figure 1).

The orange paint PO, which showed greater total colour variation after natural ageing, showed a similar trend after accelerated ageing (ΔE = 7), with an important contribution of both hue parameters a* and b*, coherent but non-rigorously homogeneous along the surface of the mockups. As stated previously, the decrease in these values is ascribable to a partial fading of PY3/74/83 and PO43 identified and to progressive degradation of the binder as well (as follows).

On the contrary, the quartz paint FR performed better with accelerated ageing (ΔE = 1) compared to outdoor natural conditions (ΔE = 3). The variation detected was contained and close to the threshold of detection for the human eye, as some areas painted with FR did not turn to other colouration, at least to the naked eye when observed in situ (Figure 8).

Additionally, the total colour variation for magenta and the golden paints (MA and OM) overcame the threshold of eye detection. As for NF, changes in MA paint can be ascribable to pigment variations with a contribution of the binder. In the case of OM, though, surface oxidation of metal powders (mainly composed of Al, Cu and Fe particles as detected by XRF) might have occurred as well, due to the synergic effect of the selected ageing conditions: this might justify the decrease in terms of L*, a consequence of a lower reflectivity of the surface because of the presence of oxidation products [59,60]. The low stability of the gold spray paint was highlighted in situ on the "Two dragons carrying a new creature artwork": the golden rays are now totally disappeared (Figure 9).

Indeed, differences in acquisition in SCI or SCE modalities are usually linked with different reflective conditions of the surface. Only in the case of PO, SCI and SCE acquisition were different in the recorded values, with a slightly higher variation in the SCI mode ascribed to a slightly more opaque surface.

As concern chemical variations induced by the most severe ageing conditions of the climate chamber, some considerations can be made related to the several degradation processes experimentally observed on the paint films.

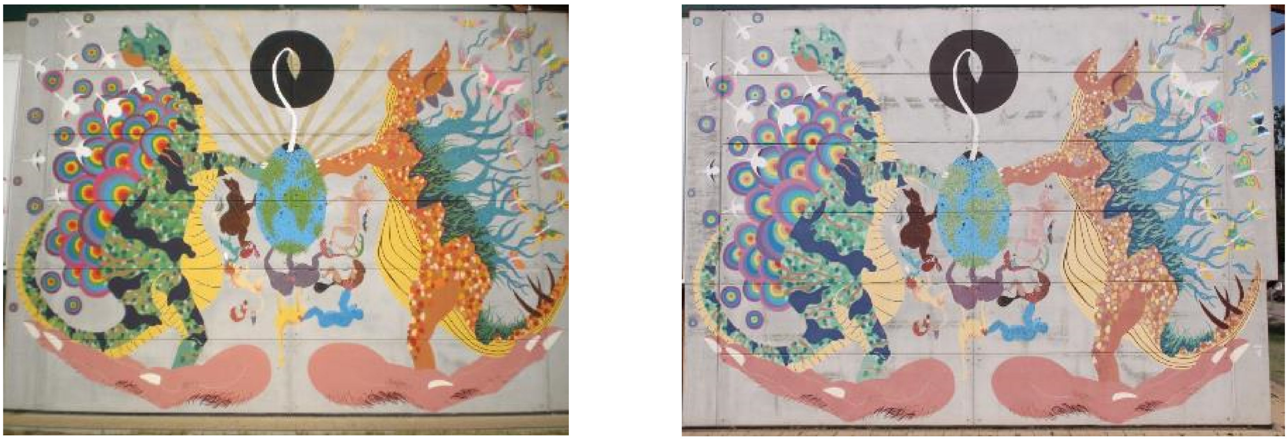


Figure 9. "Two Dragons Carrying a new creature" by Gola Hundun in 2012 (**left**) and 2019 (**right**); general chromatic alteration and fading.

Again, the most degraded case was the orange paint PO, characterised by a polystyrene–acrylic binder combined with nitrocellulose and oil-modified alkyd resin, coloured by a mixture of alizarin pigments. Through the comparison of IR spectra before and after ageing (Figure 5), a significant decrease in the main IR absorptions related to nitrocellulose (i.e., 1646, 1276 and 836 cm^{-1}) was registered. This degradation process, known as denitration, was observed already after 620 h of the experiment, and at the end of the test, also the pyranose structure showed a partial degradation, with a decrease in the related absorption at 917 cm^{-1} [61]. Py-GC/MS analyses showed in parallel a progressive decrease in the main plasticiser (DEHA) and benzoic acid: the former is ascribable to the plasticiser migration to the surface, whereas the latter is linked with chemical changes of the binder. Both the alkyd component and the styrene–acrylic one produce benzoic acid along their degradation pathways fraction [58,62]: since this compound is highly volatile, the decrease can be explained as a progressive separation from the bulk confirming the sensitivity of this commercial formulation to the selected ageing conditions.

The fluorescent paint NF contains acrylic copolymers and nitrocellulose as well; on the latter component, the ageing promoted a more evident photooxidation: the carbonyl peak (1727 cm^{-1}) showed to be broader and shifted slightly towards lower wavenumbers, an occurrence which can be justified by the formation of unsaturated ketones [63]. During this step, in this case, the formation of hydroxyl groups was promoted as well (band at 3100, peaks at 1117 and 614 cm^{-1}, from shoulder to well-readable absorption signals). Moreover, the spectrum recorded after 1240 h showed the decrease in several sharp peaks mostly linked with the colourant agent (such as those at 1316, 810, 705, 689, and 661 cm^{-1}). The more evident change identified in the Py-GC/MS results of the aged samples is the progressive decrease in the number of triazine moieties and a shift in their retention time, suggesting that a chemical change occurred to the colourant molecules, such as the loss of chromophores sites, i.e., the opening of double bonds. This result can further explain the great ΔE recorded for this formulation at the end of the accelerated ageing test.

The quartz-based red paint FR showed a certain stability from a chemical point of view. After 620 h, a slight decrease in the IR absorption of the carbonyl peak (1730 cm^{-1}) associated with the rise of a signal at 1770 cm^{-1} was observed as a clue of the beginning of the oxidation process of the acrylic resin and the production of lactones [53,54]. Nevertheless, these oxidation products were not anymore detected after 1240 h; this faintness of lactones during ageing experiments, already observed in other studies [64], is likely due to their instability [57]. As for the natural ageing, a decrease in the intensity of the polymeric pattern was registered, both in the FTIR spectra and in the Py-GC/MS data, where a significant decrease in the oligomers was progressively observed.

For the metallic paint OM, progressive development of alcoholic and oxidised species was observed in the IR spectra: in particular, an increase in the OH band at high wavenumbers and a decrease in the peak of C=O (1723 cm^{-1}) and the C-O (1143 cm^{-1}) were registered. After 1240 h, an increase in the unsaturation-related absorption along the backbone was observed as well (1649 cm^{-1}). Thus, the main degradation process started is the radical scission of the acrylic polymer. The acrylic fraction, in general, seemed to be washed away, as suggested by the progressive lower concentration of its moieties as highlighted by the Py-GC/MS results. At the same time, a decrease in plasticisers (DEP, DBP, and DIBP) was observed. It is known that in polymeric films, phthalates can migrate from bulk to the surface [55,56], so even in this case, they could have been progressively washed away during the ageing steps. As a consequence of the plasticisers loss/reduction, the mechanical performance of the paint layer was reduced, and the layer itself became thinner.

FTIR spectra of the magenta formulation MA showed a general decrease in the IR signals attributed to the binding media. The band ascribable to OH groups at 3300 cm^{-1} was observed in the spectrum recorded after 620 h of accelerated ageing, but its presence was not detected after 1240 h. The pyrograms showed a clear degradation of the alkyd resin, mainly due to photo oxidation (Figure 10). As reported for the naturally aged film, the lipidic fraction showed an increase in the concentration of oxidation products (in particular dicarboxylic acids such as suberic, azelaic and sebacic), a decrease in unsaturation (i.e., oleic acid) and the presence of oxidised (epoxy-, oxo-, and methoxy-) octadecanoic fatty acids (Table 4). A progressively higher concentration of phthalic acid was detected as well. With respect to natural ageing, these chemical variations were amplified.

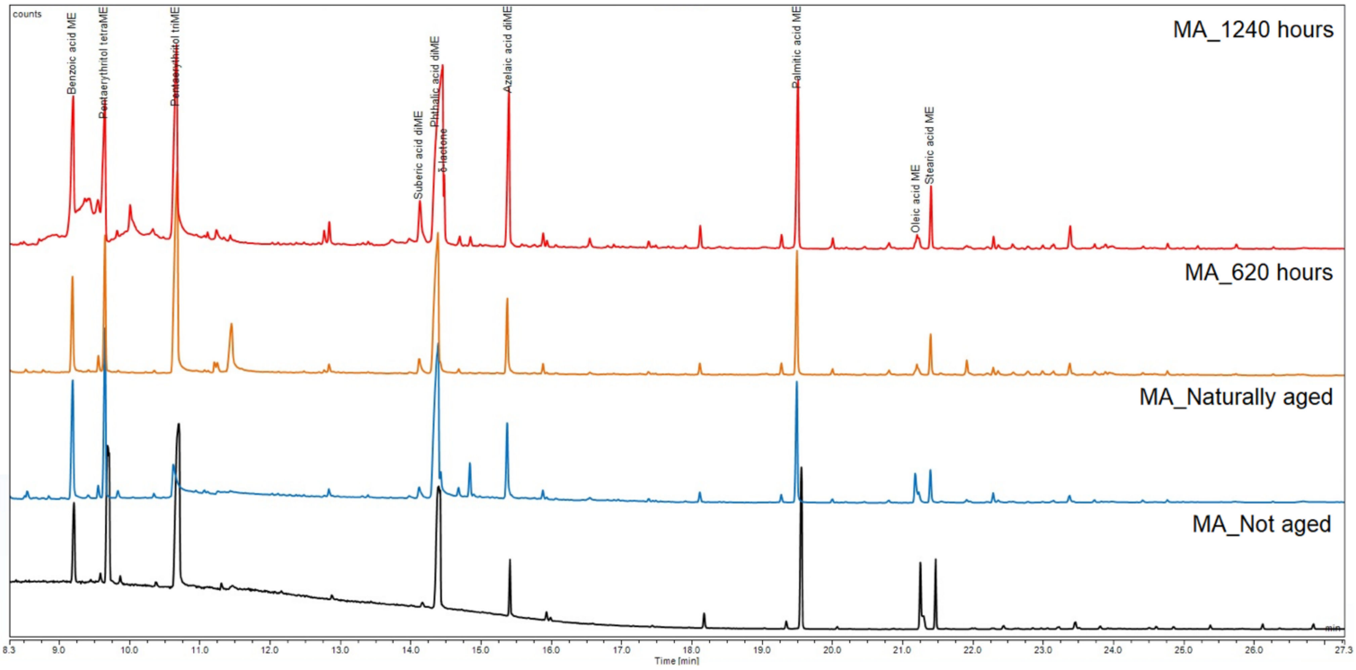


Figure 10. Pyrograms of MA films before (lower) and after natural (blue line) and accelerated (orange line for the 620 h and red line for the 1240 h steps, respectively) ageing.

The evaluation of the wettability after the accelerated ageing test did not identify any trend associable uniquely to the nature of the binder or the ageing method.

A common aspect is that, concerning accelerated ageing, paints without nitrocellulose showed an increase in θ values (i.e., FR, MA, and OM). The different oxidation paths that occurred to the orange PO paint in the ageing tests can explain the opposite behaviours recorded: when the nitrocellulose component is the most compromised, the affinity with water is increased. The greater affinity with water (lower θ values) showed as well by the fluorescent paint can be explained by the high inorganic fraction (mainly composed of hydrophilic materials, such as talc), which, with the degradation of the polymeric fraction, is even more exposed to the liquid, offering a rougher surface.

3.3. Anti-UV Protective Varnishes Performances

3.3.1. Characterisation and Chemical Resistance to Ageing Tests of Anti-UV Varnishes

Table 6 reports the main components identified in the anti-UV varnishes selected as coatings.

The acrylic-based varnish (Anti-UV 1) is composed of copolymers modified with fatty acids and plasticised with dimethyl adipate (DMA) and polyethylene glycol (PEG). The presence of 2-ethylhexyl acrylate acid 2-EHA among the monomers ensures good adhesion and chemical resistance properties of the resulting film [65]. Cellulose nitrate was not identified.

The second product (anti-UV 2) contains a drying-oil modified alkyd resin (the pyrogram showed benzoic acid, pentaerythritol, phthalic acid, numerous saturated mono-fatty acids, di-fatty acids and unsaturated fatty acids) flanked by an acrylic (MA-MMA) and vinyl acetate–vinyl versatate (VA-VeoVA) copolymers to improve the mechanical and adhesive properties and chemical resistance to UV-light [66–69]. PEG was identified in the latter case as well.

Table 6. Summary of anti-UV varnishes chemical characterisation; identified compounds are classified into categories.

Sample Name	Binder(s)	Additives	TGA Residue 700 °C [%]	Comments
Anti-UV 1	Acrylic copolymer (MA, MMA, nBA, 2EHA, EMA)	Urea-formaldehyde Fatty acids DMA Methyl ethyl adipate 1,3 Propanediol PEG	14.3	Among the comonomer, 2-ethyl hexyl acrylate, whose addition can provide flexibility, water resistance, good weathering characteristics, and UV-light resistance [65,70]
Anti-UV 2	Oil (drying oil) and acrylic-modified alkyd resin VA-VeoVa	Isobutyl methyl phthalate Benzaldehyde PEG	6.6	

The acrylic formulation (Anti-UV 1) revealed to be resistant to environmental agents as supported by the spectroscopic analyses; the film resulted in being more stable under controlled conditions, showing only a slight increase in the shoulder at 1645 cm^{-1} linked, as reported above, with a greater number of unsaturations along the olefinic chain as a consequence of the photolytic chain scission. At the end of the natural ageing, the same phenomenon was observed, with the relative higher intensity of the peak at 877 cm^{-1}, characteristic of the side methyl of PMMA (CH_3 rocking) [71].

The alkyd-based formulation (Anti-UV 2) showed in its FTIR spectra after accelerated ageing a progressive decrease in the C-O stretching vibration peak at 1253 cm^{-1} and, after 1240 h of ageing, a slight broadening of the carbonyl peak at 1717 cm^{-1}, suggesting the beginning of photo-oxidation. After natural ageing, the spectrum showed only a general increase in the baseline, which was explained as a thinning of the film along the glass slide surface. This morphological change was recorded for all samples.

Considering the colorimetric aspect (Table 7), the formulations behave very similarly, slightly differing only in the b* component. The natural ageing affected L* and b*, without inducing a visible change ($\Delta E = 2$ and 1 for Anti-UV 1 and 2, respectively). The severest ageing conditions caused a clear variation of the alkyd varnish ($\Delta E = 5$) influenced by the decrease in b*, suggesting a yellowing phenomenon, aligned with the detected broadening of the carbonyl peak in FTIR spectra.

Table 7. Colorimetric data before and after ageing tests of anti-UV coatings films.

	Anti-UV 1			**Anti-UV 2**		
	L*	**a***	**b***	**L***	**a***	**b***
Before ageing	89	1	−7	89	1	−4
	dL*	**da***	**db***	**dL***	**da***	**db***
After natural ageing	−1	0	2	−1	0	1
After accelerated ageing	−2	0	2	−2	−1	4

3.3.2. Colorimetric and Surface Changes Feature of Paints after Anti-UV Varnish Application

The application of the anti-UV varnishes, as expected, changed the surface features of the paint layers, from both colorimetric and hydrophilicity aspects. The presence of a coating induced a slight darkening of the lower layer (decrease in L*, promoting a higher saturation of the colour above 560 nm (Figure 11) and a higher gloss of the surface, Table 8) and caused a different appearance, especially when the paint had a peculiar aesthetical feature, such as a fluorescence or metallic aspect (i.e., NF and OM). On both NF and OM paints, the alkyd varnish was applied, and the main influence referred to a decrease in the b* parameter; the difference was detectable for NF (ΔE = 7).

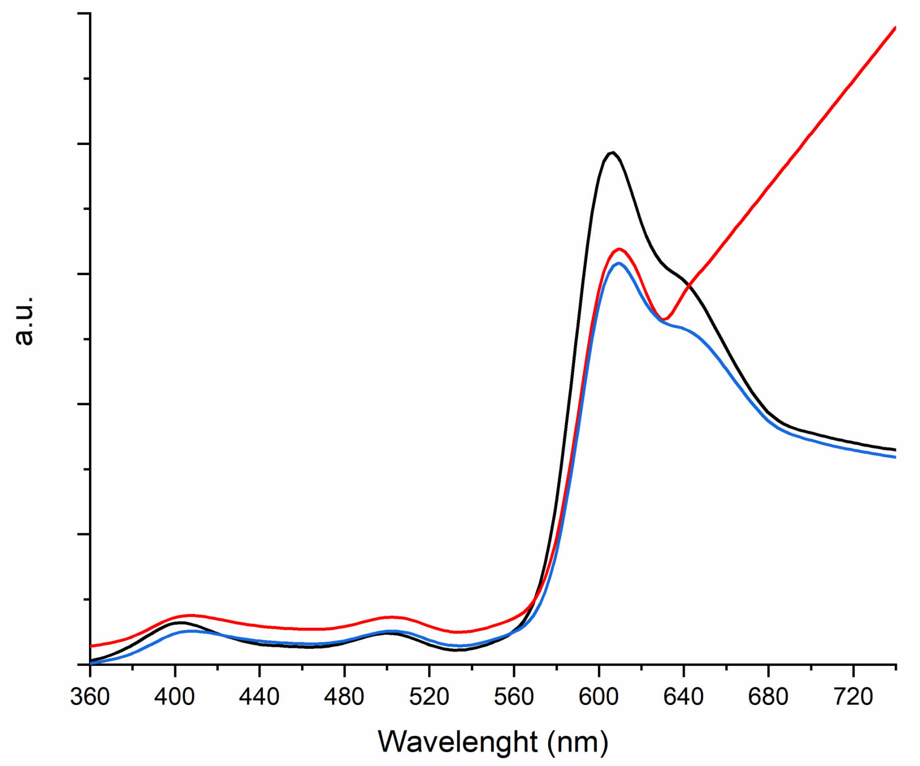


Figure 11. Reflectance spectra of NF paint before (black line, SCI and SCE overlapped) and after anti-UV varnish application (red line-SCI, and blue line-SCE); a general higher saturation was observed at a wavelength above 560 nm, in the orange-red region; the increase in gloss is here observed as higher reflectance level compared to the other spectra and a final drift in the SCI curve; despite that, the paint layer maintained its typical spectral feature.

Table 8. Colorimetric data of the aesthetical appearance of paint layers after the application of the anti-UV coatings.

Colorimetric Variations																
Anti-UV Applied	**AV1**				**SV1**											
	PO				**NF**				**MA**				**OM**			
	dL*	**da***	**db***	**ΔE**	**dL***	**da***	**db***	**ΔE**	**dL***	**da***	**db***	**ΔE**	**dL***	**da***	**db***	**ΔE**
	−1	0	0	1	−2	2	−6	7	0	0	0	0	−1	−1	−2	2

Despite the chemical composition of the varnish, its application saw a generalised decrease in θ values, thus leading to more hydrophilic surfaces (Table 9).

Table 9. Wettability evaluation of painted surfaces after the application of the anti-UV coatings (contact angle measurements, θ values recorded and differences to the initial situation).

Contact Angles θ and Differences				
Anti-UV Applied	**AV1**	**SV1**		
	PO	**NF**	**MA**	**OM**
	79 (−20)	70 (−11)	72 (−17)	66 (−8)

4. Discussion

It is worth noticing how, despite similar ageing times and average values of temperature and relative humidity above reported, the effect of the interaction of the degradation agents is not predictable and easy to be interpreted, even though, especially during the accelerated ageing test, it is well controlled. Accelerated ageing experiments are often performed to test products and compounds chemical stability. Nevertheless, there is not a general rule about the parallelism with natural ageing and real degradation kinetics, since these depend on the artworks' real location, in terms of world place and consequent direct exposure to the environmental factors. This study considered only three months of natural ageing, though observing already noteworthy changes and thus giving reason to this short time.

Indeed, all paint formulations, no matter their chemical composition, showed clues of chemical changes that occurred during the ageing tests. Natural ageing performed during the winter season saw cold temperatures and quite high relative humidity: from the obtained results, it is possible to affirm that these two parameters most affected the samples. On the contrary, using a climate chamber allowed the most prolonged and controlled exposition to UV light (1000 h in total) and the interaction of important conditions, such as RH 95% and T 45 °C occurred for quite a long time (240 h in total).

While, after three months of exposure to natural outdoor agents, the observed effects may be partially attributed to further curing of the polymer film, the results obtained may also suggest how the season in which the murals are painted may influence the final appearance and perspective of the artwork. Indeed, a formulation such as the orange paint PO showed already, after three months outdoors, a colorimetric change detectable by the human eye, which found its confirmation in the chemical changes observed after FTIR and Py-GC/MS analyses.

Emblematic is also the case of the fluorescent paint NF, which showed the highest ΔE variations due to the light fastness of organic pigments: at the end of the accelerated ageing, it was not recognizable anymore, reaching the aesthetical degradation level observed in the real case in Reggio Emilia.

PO and NF paints have a similar composition, with an acrylic-based binder with nitrocellulose. However, the addition of alkyd resin to PO formulation made it more susceptible to chemical changes under natural conditions when this was most probably linked with the reticulation of this resin and to the effect of humidity; on the contrary, at the end of the accelerated test, nitrocellulose was the component which most underwent degradation. Moreover, pigments can facilitate degradation issues [53,72,73]: azo-pigments in particular, that give colour to this paint, are known to promote degradation of the binder [53] and this study seems to confirm it. Concerning the binder, similar occurred to NF, where this trend was observed by chemical analyses. The label on its canister indicates low stability to UV light, information linked mostly to the colour lightfastness; nevertheless, the low binder-to-pigment concentration (less than 3% of organic fraction, which counts besides the binder all organic additives as well, such as the fluorescent triazine-based colouring agent, plasticisers and stabilisers) was at the base of the fragility developed with loss of the mechanical properties, which made the final state of the paint layer more severe.

The greater amount of binding media (ca 30 ÷ 85%) in the other formulations ensured good adhesion to glass slide surfaces within the research tests.

A decrease in the plasticisers amounts at the end of the test, both natural and accelerated, was often registered: plasticisers may easily migrate toward the surface through the macromolecular structure of the polymeric film; even though deposition of these molecules along the surface was not detected, rain or drops due to condensation of water over the paint layer could promote their removal, followed by a depletion of the mechanical properties over time. The golden OM and the quartz-based FR paints showed similar behaviour, with a progressive loss of phthalates during natural and accelerated ageing.

Other than plasticisers, OM and FR paints showed a decrease in the concentration of the oligomers of the acrylic resin: since they remained after the curing process, the hypothesis is that, other than a cross-linking phenomenon, leaching of this relative movable fraction or erosion of the binder occurred as well [6,11,13,74]. This finding might also be confirmed from the relative concentration between organic/inorganic fractions in FTIR spectra, where calcite absorption showed relatively higher intensity. An erosive phenomenon of the binder was reported in the literature as a chalking effect, linking it to the presence and loss of titanium oxide [11,75], but also to a photolytic degradation of the binder itself [76,77]. In this study, only the golden paint has TiO_2 as filler, whereas the quartz paint is based on silicate and carbonate only. At the end of the experiment, FTIR spectra showed silicates in lower concentrations compared to the initial state, and the loss might be related to the loss of oligomers. Despite that, the complexity of the considered formulations makes it difficult to describe deeply what was observed.

Where a lipidic fraction was present (PO and MA paints), changes were observed already in natural ageing conditions. In particular, the higher amount of azelaic acid is the evidence of oxidation and curing, whereas the greater exposition to UV-light during the artificial ageing test saw a significant decrease in the unsaturated oleic acid already at the end of the first step (620 h), due to stronger oxidation.

Similarly, between the two anti-UV varnishes tested, the alkyd-based one showed a progressive development of oxidised species and a progressive colour change. The acrylic coating was more stable. In both cases, though, the colour variation was limited, due to the positive effect of UV-stabilisation of the formulations, which is mainly conferred by a selective choice of the binder components, such as 2-EHA or VeoVA.

Their application on paint layers affected the visual appearance, especially as the interaction between paint and natural light plays an important role in the aesthetical aspect, and thus on the message of the artwork itself. Such is the case of the fluorescent NF and the golden OM spray paints, whose smoother surface due to the application of the coating showed a greater ΔE (7 and 2 respectively). Besides the colorimetric changes, the application of the anti-UV varnishes caused a decrease in the hydrophobicity of the surface. If, from one side, differences in contact angle and SCI/SCE recorded values might be ascribed to the presence of additives at the interface or micro-roughness not perceivable by the portable microscope, from the other side, a systematic variation of the wettability should be more investigated to understand if it can promote leaching and/or erosion of the coating itself, reducing its efficacy and requesting its constant renovation.

5. Conclusions and Further Perspectives

The multi-analytical approach pursued in the study of commercial paints formulations, used by the Proyecto Ritual collective and by Gola Hundun, Ivan Pontevia and Daniele Castagnetti in the realisation of their urban artworks, allowed the follow up of their degradation under natural and accelerated ageing tests. Acrylic-based binders confirmed their greater stability compared to alkyd resins and nitrocellulose resins; nevertheless, the complex chemical composition of these products in terms of their chemical nature and relative concentrations makes a general conclusion about the degradation kinetics and dynamics difficult to be formulated. In general, the presence of UV-light stabilisers in formulations might help the resistance to sunlight exposure of the binder and the other compounds dispersed, but despite that, most of the paints showed a certain instability, showing, in some cases, already after a few months of natural ageing, the development of degradation processes.

A practical consideration that emerges from this research is that the application of an anti-UV varnish on top of the paint layers can promote easier and longer conservation of urban art, only partially scarifying the aesthetical feature of the coloured varnishes. The characterisation of the selected varnished used as coatings showed greater stability of these films compared to the spray paints, and the first insight of their compatibility was documented.

The application of anti-UV systems can be suggested to urban and street artists and festival organisation committees, highlighting this as an important preservation tool of the artworks. In the meantime, scientific research needs to continue with the stability testing of layered systems, which should also consider other chemical classes of polymers used in commercial formulations, different types of pigments, and even the application of possible anti-graffiti and other classes of coatings to protect these sometimes too-fugitive works of art.

Author Contributions: Conceptualisation, F.C.I., I.S. and M.B.; methodology, F.C.I., D.C., I.S. and M.B.; formal analysis, R.L., D.C. and F.C.I.; resources, F.C.I., I.S. and M.B.; data curation, D.C., F.C.I. and R.L.; writing—original draft preparation, D.C., R.L. and F.C.I.; writing—review and editing, D.C., F.C.I., R.L., I.S. and M.B. All authors have read and agreed to the published version of the manuscript.

Funding: Part of this research was funded by the European Commission, Program Erasmus Plus, Key Action 2, Cooperation for innovation and the exchange of good practices—Knowledge Alliance 2017, Project No. 588082-EPP-A-2017-1-IT-EPPKA-KA. The European Commission's support for the production of this publication does not constitute an endorsement of the contents, which reflect the views only of the authors, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: Francesca C. Izzo would like to thank the Municipality of Venice for its support of the research through the "Patto per la Città di Venezia". The authors thank Elettra Ferrari Mazzanti of the AN.T.A.RES team for samples preparation and her help in the different phases of the project; her activities were financed by the CAPuS project.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Figure A1. Spray cans of MNT 94 colour line supplied by Montana® Colours—Spain.

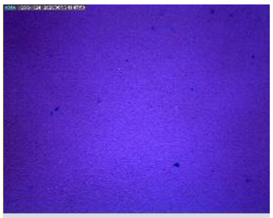
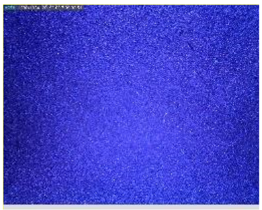
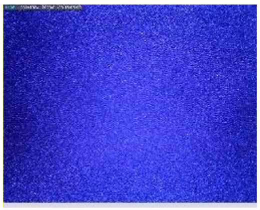
Figure A2. One of the realisation phases of the artwork "Economy subdues you" by Zosen, Reggio Emilia, Italy, 2010.

Appendix B

Table A1. Pictures acquired with a digital microscope under visible (Vis) and UV-light before and after both, natural and accelerated ageing.

Paint Film	Acquisition Light Condition	Before Ageing	After Natural Ageing	After Accelerated Ageing
PO	Vis			
	UV			
NF	Vis			
	UV			
FR	Vis			
	UV			

Table A1. *Cont.*

Paint Film	Acquisition Light Condition	Before Ageing	After Natural Ageing	After Accelerated Ageing
MA	Vis			
	UV			
OM	Vis			
	UV			

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